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L1 STRUCTURE UPLOADED

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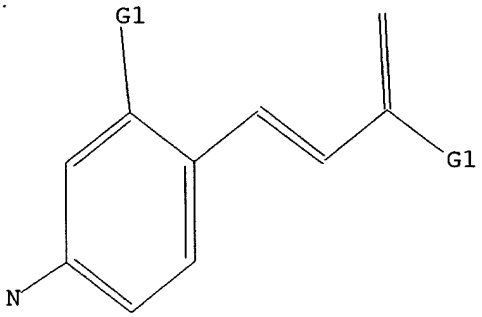

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Structure attributes must be viewed using STN Express query preparation.

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Substance data SEARCH and crossover from CAS REGISTRY in progress...
Use DISPLAY HITSTR (or FHITSTR) to directly view retrieved structures.

FULL SEARCH INITIATED 12:41:39 FILE 'REGISTRY'
FULL SCREEN SEARCH COMPLETED - 1226 TO ITERATE

100.0% PROCESSED 1226 ITERATIONS 769 ANSWERS
SEARCH TIME: 00.00.01

L2 769 SEA SSS FUL L1

L3 114 L2

=> s l3 and py<2001
20846900 PY<2001
L4 92 L3 AND PY<2001

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=> s 80-92 ibib abs hitstr
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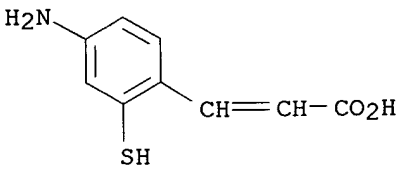
L4 ANSWER 80 OF 92 CAPLUS COPYRIGHT 2005 ACS on STN
ACCESSION NUMBER: 1959:45191 CAPLUS
DOCUMENT NUMBER: 53:45191
ORIGINAL REFERENCE NO.: 53:8131i,8132a-i,8133a
TITLE: 2-Nitro-4-aminobenzaldehyde and thiocoumarin derivatives. I
AUTHOR(S): Ricci, Adolfo
CORPORATE SOURCE: Univ. Perugia, Italy
SOURCE: Annali di Chimica (Rome, Italy) (**1958**), 48, 985-96
CODEN: ANCRAI; ISSN: 0003-4592
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
GI For diagram(s), see printed CA Issue.
AB cf. C.A. 51, 16454i. Preparation of derivs. of 2,4-O2N(H2N)C6H8CHO (I) is described; these are to be tested for bacteriostatic properties. Cyclization of 2,4-HS(H2N)C6H3CH:CHCO2H (II) gives 7-aminothiacoumarin (III) from which a series of fluorescent thiacoumarins are prepared These are being tested for photo-dynamic activity and action against paramecium. 2,4-O2N(AcNH)C6H3Me (10 g.) in 80 cc. Ac2O and 100 cc. AcOH cooled to 0°, treated slowly with 11 cc. H2SO4 below 10° then with 14 g. CrO3 in 80 cc. Ac2O at 15-20°, kept 1 hr., and drowned in ice H2O ppts. 50% 2,4-O2N(AcNH)C6H3CH(OAC)2, m. 146-7°, hydrolyzed by HCl in aqueous EtOH to 85% I, m. 140-1°. A high-melting, insol. polymer of I is precipitated at the same time and during recrystn. of I. I (5 g.) and 2 g. MeNO2 in EtOH at -5° is treated with 3.5 g. KOH in 6.5 cc. H2O and 65 cc. EtOH, kept 15 min. at -5°, then filtered to give 2,4-O2N(H2N)C6H3CH(OH)CH2NO2, m. 138-45° (unstable), boiled 5 min. with 2 g. NaOAc and 20 cc. Ac2O then drowned in H2O to give 2,4-O2N(AcNH)C6H3CH:CHNO2, m. 187-8° (decomposition). I (10 g.) added to 8 g. barbituric acid in 80 cc. H2O gives a black precipitate, insol. in most solvents, extracted with dioxane to leave yellow 5-(2-nitro-4-aminobenzylidene)barbituric acid, not m. 360°. I forms a thiosemicarbazone (IV), m. 255-6°. IV (2 g.) is refluxed several hrs. with 0.9 g. succinic anhydride in xylene, cooled, filtered, the precipitate dissolved in hot Na2CO3, and cooled to precipitate the Na salt of 2-nitro-4-(succinylamino)-benzaldehyde thiosemicarbazone; the free acid, m. 228° (decomposition). IV (2 g.) refluxed 12 hrs. in EtOH with 0.8 g. ClCH2CO2H and 1.6 g. NaHCO3, concentrated, diluted with H2O, and acidified ppts. 2,4-O2N(HO2CCH2NH)C6H3CH:NNHCSNH2, m. 279° (decomposition). I (5 g.) in 20 cc. HCO2H is treated with 8 ml. concentrated HCl, diazotized at 0° with 2.1 g. NaNO2 in H2O, the solution poured into 3.6 g. CuSCN and 17.5 g. KSCN in a min. of H2O, heated to complete the reaction, diluted with 10 vols. H2O, and filtered to give 2,4-O2N(NCS)C6H3CHO, m. 108°. Reduction of 5 g. I in hot aqueous EtOH by 60 g. FeSO4 and 30 ml. NH4OH at 60-70° gives 35-40% 2,4-(H2N)2C6H3CHO, m. 152° (thiosemicarbazone, m. 225-6°). I (10 g.) and 10 g. CH2(CO2H)2 in 25 cc. EtOH is refluxed 4 hrs. with 1 ml. pyridine, filtered, and the filtrate concentrated to give a 2nd crop of 2,4-O2N(H2N)C6H3CH:CHCO2H, m. 255-6° (decomposition); Ac derivative, m. 280-1° (decomposition). This (2 g.) in 6 cc. HCl is reduced at 60-70° by 3.4 g. Sn to 7-aminocarbostyril (V), m 290-1°. Reduction of 10 g. 2,4-O2N(AcNH)C6H3CH:CHCO2H by FeSO4-NH4OH gives 2,4-H2N(AcNH)C6H3CH:CHCO2H (VI), m. 228° (decomposition), hydrolyzed by acid to V. VI (10 g.) in 50 cc. HCO2H (d. 1.20) is treated with 11.5 cc. HCl (HCl salt precipitated), diazotized, and poured into a solution of 6 g. CuSCN and 27 g. KSCN to give 2,4-NCS(AcNH)C6H3CH:CHCO2H, m. 207-8°. This (5 g.) is treated with 1.7 g. NaHCO3 in a little H2O, then with 5 g. Na2S, heated 1 hr. at 50-60°, then cooled, and acidified to precipitate II, m. 210-12°. II (5 g.) and 10 g. NaOAc is heated 1 hr. in 25 cc. Ac2O, diluted with H2O, kept several hrs., filtered, the precipitate washed with warm aqueous Na2CO3 and H2O, dissolved in boiling dilute HCl, the solution concentrated, and cooled to precipitate III.-HCl, filtered off, dissolved in H2O, and treated with NaHCO3 to precipitate III, m. 176-7°, volatile in steam. III (2 g.) dissolved in hot H2O

containing 3 cc. concentrated HCl, cooled, diazotized, poured into 1.2 g. CuCl in concentrated HCl, diluted and heated, then made alkaline, and steam distilled gives 7-chlorothiacoumarin, m. 136.5°. Similarly are prepared 7-iodo-(m. 141-2°) and 7-cyanothiacoumarin (m. 231-2°). III (2 g.) in 4 cc. HCO_2H is treated with 1 cc. concentrated H_2SO_4, diazotized, poured into 1.6 g. CuBr in concentrated HBr, diluted, heated, and filtered to give 7-bromothiacoumarin, m. 105-6°. 7-Thiocyanothiacoumarin, m. 154-5°, is prepared similarly. III (2 g.) is dissolved in 2 cc. concentrated H_2SO_4 in 100 cc. hot H_2O, cooled, diazotized, heated slowly to 70-80° and finally refluxed then cooled to precipitate 7-hydroxythiacoumarin, m. 231-2°. This is methylated by MeI in 2N KOH to 7-methoxythiacoumarin, m. 108° (30% unchanged compound recovered). III (2 g.) in 10 cc. AcOH is treated with 2.3 g. powdered KSCN then dropwise with 0.6 ml. Br in 10 ml. AcOH, kept 30 min., then poured into 200 ml. H_2O. The precipitate (a mixture of 6(?)-thiocyano-7-aminothiacoumarin and VII) is boiled with 2N HCl, concentrated, and made alkaline with Na_2CO_3 to precipitate VII, m. 293-4°.

IT **99357-80-9**, Cinnamic acid, 4-amino-2-mercapto- **100060-72-8**, Cinnamic acid, 4-acetamido-2-amino- **117000-64-3**, Cinnamic acid, 4-acetamido-2-thiocyanato-
(preparation of)

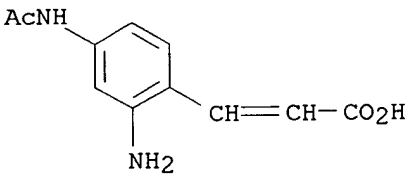
RN 99357-80-9 CAPLUS

CN Cinnamic acid, 4-amino-2-mercapto- (6CI) (CA INDEX NAME)



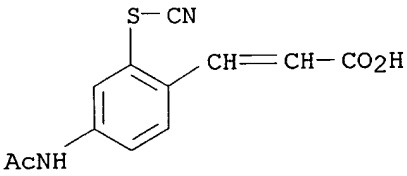
RN 100060-72-8 CAPLUS

CN Cinnamic acid, 4-acetamido-2-amino- (6CI) (CA INDEX NAME)



RN 117000-64-3 CAPLUS

CN Cinnamic acid, 4-acetamido-2-thiocyanato- (6CI) (CA INDEX NAME)



L4 ANSWER 81 OF 92 CAPLUS COPYRIGHT 2005 ACS on STN

ACCESSION NUMBER: 1959:41180 CAPLUS

DOCUMENT NUMBER: 53:41180

ORIGINAL REFERENCE NO.: 53:7423e-f

TITLE: Antibacterial potency of styrene derivatives I

AUTHOR(S): Ricci, Adolfo; Angeletti, Pietro U.

CORPORATE SOURCE: Univ. Perugia, Italy

SOURCE: Bollettino Chimico Farmaceutico (**1958**), 97, 662-7

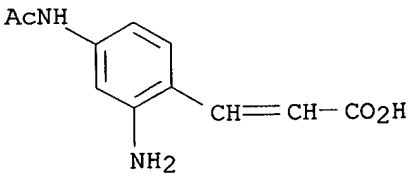
CODEN: BCFAAI; ISSN: 0006-6648
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

AB 2-Nitro-4-acetamido-β-nitro-styrene (I) was bacteristatic against Staphylococcus aureus at concns. of 5 γ/ml., which activity increased by increased concentration to 15 γ/ml. The organisms were completely inhibited at higher concentration of I after 18 hrs. of incubation. The substance was less effective against Escherichia coli. Three cinnamic acid derivs. had insignificant activity. Intraperitoneal injections of 20 mg./kg. I in mice were well tolerated.

IT **100060-72-8**, Cinnamic acid, 4-acetamido-2-amino-
(effect on bacteria)

RN 100060-72-8 CAPLUS

CN Cinnamic acid, 4-acetamido-2-amino- (6CI) (CA INDEX NAME)



L4 ANSWER 82 OF 92 CAPLUS COPYRIGHT 2005 ACS on STN

ACCESSION NUMBER: 1958:92937 CAPLUS
DOCUMENT NUMBER: 52:92937
ORIGINAL REFERENCE NO.: 52:16373f-g
TITLE: p-Aminocoumaric acid
INVENTOR(S): Libermann, D.
PATENT ASSIGNEE(S): Chimie et atomistique
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

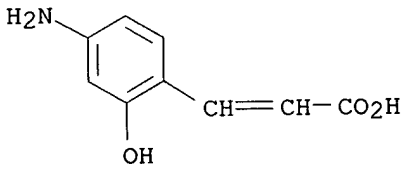
PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
FR 1057860		19540311	FR	<--

AB p-Aminocoumaric acid (I) is useful as a bacteriostatic and tuberculostatic agent in veterinary medicine. Thus, 2.5 g. Na is dissolved in 15 ml. EtOH, and 1.6 g. 7-aminocoumarin is added. After 10 min. refluxing, the solution is allowed to stand several hrs. at room temperature, evaporated at room temperature, and the residue taken up in H2O and acidified by AcOH. The precipitate is dissolved in dilute NH3 and repptd. with AcOH to give I, m. 181° (decomposition).

IT **99357-85-4**, Cinnamic acid, 4-amino-2-hydroxy-
(preparation of)

RN 99357-85-4 CAPLUS

CN Cinnamic acid, 4-amino-2-hydroxy- (6CI) (CA INDEX NAME)



L4 ANSWER 83 OF 92 CAPLUS COPYRIGHT 2005 ACS on STN

ACCESSION NUMBER: 1958:92936 CAPLUS
DOCUMENT NUMBER: 52:92936
ORIGINAL REFERENCE NO.: 52:16373d-f
TITLE: 3,5-Dioxopyrazolidine derivatives

INVENTOR(S): Wiedemann, O.
PATENT ASSIGNEE(S): J. R. Geigy A.-G.
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

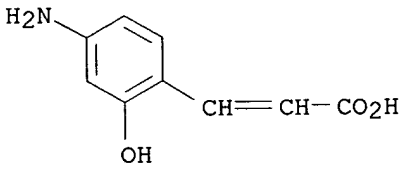
PATENT NO.	KIND	DATE	APPLICATION NO.	DATE	
IL 9097		19560913	IL		<--

AB The title compds. are prepared by treating a reactive derivative of a monosubstituted malonic acid with a metal organic compound of an azobenzene at room temperature or by heating under reflux. EtBr (30.5 g.) in 60 ml. absolute ether was slowly added to 6.8 g. Mg in 20 ml. ether, the mixture boiled under reflux 30 min., treated dropwise with 25.5 g. (PhN:)2 in 200 ml. absolute ether while cooling in ice H2O, repeatedly shaken, boiled for 30 min. more under reflux, and cooled to -10° to give a pale brown powder. Butylmalonyl chloride (I) (27.6 g.) in 200 ml. absolute ether was added slowly at 0-5° with shaking, to this mixture, the whole boiled 2 hrs. under reflux and left standing for a day, to give a mixture containing a tough brown resin in the ether solution Acidifying and working up gave after recrystn. from alc. 1,2-diphenyl-3,5-dioxo-4-butylpyrazolidine, m. 106°, also obtained by treating I with N,N'-di-lithiohydrazobenzene.

IT **99357-85-4**, Cinnamic acid, 4-amino-2-hydroxy-
(preparation of)

RN 99357-85-4 CAPLUS

CN Cinnamic acid, 4-amino-2-hydroxy- (6CI) (CA INDEX NAME)



L4 ANSWER 84 OF 92 CAPLUS COPYRIGHT 2005 ACS on STN
ACCESSION NUMBER: 1957:74459 CAPLUS
DOCUMENT NUMBER: 51:74459
ORIGINAL REFERENCE NO.: 51:13409g-i,13410a-b
TITLE: Methine dyes for synthetic fibers
INVENTOR(S): Kartinos, Nicholas J.; Normington, James B.; Williams, Wm. W.
PATENT ASSIGNEE(S): General Aniline & Film Corp.
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE	
US 2789125		19570416	US		<--

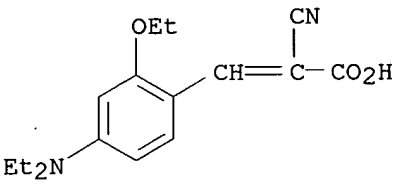
AB Products, having high tinctorial strength, excellent light-, chlorine-, and wash-fastness, good sublimation and fluorescent properties, and adaptability as fluorescent pigments and brightening agents, particularly for synthetic fibers, such as acetate rayons, are obtained by condensing a 2-substituted 4-[dialkyl- or bis(alkylcarboxyalkyl)amino]benzaldehyde with an alkyl cyanoacetate or cyanoethyl cyanoacetate in the presence of a basic or acid condensing agent. The dyes have the formula 2,4-R'(R2N)C6H3CH:C(CN)CO2CH2CH2CN, where R is a lower alkyl group, and R' is a halogen, hydroxy, or lower alkoxy group. 2-Ethoxy-4-diethylaminobenzaldehyde (I), m. 45.8°, was obtained in 38% yield by combining 96.5 g. of N,N-diethyl-m-phenetidine and 73 g. of dimethylformamide, cooling to 10°, adding 92 ml. of POCl3 dropwise during 45 min., warming on a steam bath for 4 hrs., cooling, drowning in

ice water, and adding 300 ml. of 40% NaOH solution until the pH was 3-5. By mixing 11.05 g. of I, 6.8 g. of Et cyanoacetate (II), 30 ml. of iso-PrOH (III), and 5 drops of piperidine (IV), mildly refluxing for 1 hr., collecting and drying the bright-orange solid gave Et α-cyano-4-(diethylamino)-2-ethoxycinnamate in 57% yield, m. 74-5°, and fluorescing strongly under ultraviolet light. The following derivs. of α-cyanocinnamate were also prepared: Et 4-(diethylamino)-2-hydroxy, m. 147-9°, from 2-hydroxy-4-diethylaminobenzaldehyde, m. 62°, and II; cyanoethyl 4-(diethylamino)-2-ethoxy, b0.7-0.8 150-4°, from I and cyanoethyl cyanoacetate; Et 4-(diethylamino)-2-methoxy from 2-methoxy-4-diethylaminobenzaldehyde and II; Et 4-(diethylamino)-2-chloro, m. 83.5°, from 2-chloro-4-diethylaminobenzaldehyde, b0.6 132-5°, and II; cyanomethyl 2-chloro-4-diethylamino, m. 98-100°; cyanoethyl 2-methyl-4-[bis(ethylcarboxyethyl)-amino], m. 122-4°; cyanoethyl 4-[bis(ethylcarboxyethyl)-amino], m. 104-8°; and Et 2-chloro-4-[bis(ethylcarboxyethyl)-amino], m. 64-5°. The essentially H2O-insol. dyes are applied directly to fabric as aqueous suspensions or dispersions.

IT **859922-10-4**, Cinnamic acid, α-cyano-4-diethylamino-2-ethoxy-
(esters)

RN 859922-10-4 CAPLUS

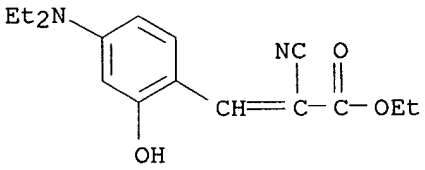
CN Cinnamic acid, α-cyano-4-diethylamino-2-ethoxy- (6CI) (CA INDEX NAME)



IT **101586-75-8**, Cinnamic acid, α-cyano-4-diethylamino-2-hydroxy-, ethyl ester **101602-91-9**, Cinnamic acid, α-cyano-4-diethylamino-2-methoxy-, ethyl ester
(preparation of)

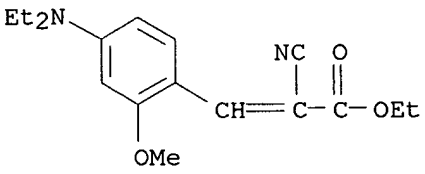
RN 101586-75-8 CAPLUS

CN Cinnamic acid, α-cyano-4-diethylamino-2-hydroxy-, ethyl ester (6CI) (CA INDEX NAME)



RN 101602-91-9 CAPLUS

CN 2-Propenoic acid, 2-cyano-3-[4-(diethylamino)-2-methoxyphenyl]-, ethyl ester (9CI) (CA INDEX NAME)



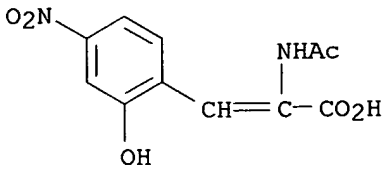
L4 ANSWER 85 OF 92 CAPLUS COPYRIGHT 2005 ACS on STN

ACCESSION NUMBER: 1957:66507 CAPLUS

DOCUMENT NUMBER: 51:66507

ORIGINAL REFERENCE NO.: 51:12035a-i
TITLE: Reactions of amino acids and peptides with aromatic aldehydes. I
AUTHOR(S): Havinga, E.; Spitzer, E. L. T. M.
CORPORATE SOURCE: Univ. Leiden, Neth.
SOURCE: Recueil des Travaux Chimiques des Pays-Bas et de la Belgique (**1957**), 76, 173-9
CODEN: RTCPB4; ISSN: 0370-7539
DOCUMENT TYPE: Journal
LANGUAGE: English
AB Formation of unsatd. azlactones by the Erlenmeyer-Plochl reaction with Ac2O as an acetylating medium and NaOAc as catalyst according to Dakin (C.A. 23, 4205), and with EtOH as solvent in the absence of a catalyst by the method of Bergmann, et al. (C.A. 46, 8637e), has been investigated. Glycine (1.5 g.) heated in 3 ml. AcOH and 2 ml. Ac2O, the clear solution treated with 1.64 g. anhydrous NaOAc, 2.2 g. BzH, and 7 ml. Ac2O, heated 2 hrs. on a water bath at 95°, cooled, diluted with H2O, and the precipitate recrystd. from C6H6 gave α-acetamidocinnamic acid azlactone, m. 152-3°, which, heated in 0.5N NaOH with C, filtered, the filtrate acidified, and the product crystallized from H2O gave PhCH:C(NHAc)CO2H, m. 195-6°. Similarly, were prepared the following RCH:C(NHAc)CO2H (R and m.p. given): p-O2NC6H4, 227-9°; p-ClC6H4, 223-4°; 2,4-HO(O2N)C6H3, 218-20° (from BuOH-petr. ether); and the corresponding azlactones, m. 182-4°, 143-5° (fluorescent in ultraviolet light), and 298-310° (from AcOH). Glycine (1.5 g.) and 3.92 g. 2,4-(O2N)2C6H3CHO treated as above, the tarry product taken up in 0.5N NaOH, the solution heated, filtered, the filtrate acidified, and the precipitate crystallized from BuOH gave 2,4-(O2N)C6H3CH:C(NHAc)CO2H, m. 205-7°. NEt3 as an alternative to NaOAc did not affect the yields. Ascending paper chromatography with 21:39.5:39.5 pyridine-BuOH-H2O as eluant was used to follow the course of the reactions, the acetamidocinnamic acids giving dark spots (cf. Rydon and Smith, C.A. 46, 11290b), also detected under ultraviolet light by fluorescence or as dark spots. No "Dakin" condensation occurred with glycine derivs. in which the CO2H group had been esterified (cf. Doherty, et al., C.A. 38, 641), though acetylalanylglycine (I) gave a crystalline product. I (1.1 g.) added to 0.9 g. p-O2NC6H4CHO and 0.9 g. anhydrous NaOAc in 10 ml. hot Ac2O and 2 ml. AcOH, the cooled mixture filtered, the crystalline product (1.44 g.) taken up in H2O, filtered, and the residue twice extracted with EtOH and crystallized from dioxane gave a crystalline condensation product, C14H13N3O5, m. 210°, orange fluorescence in ultraviolet light. The above series of aldehydes, with the exception of 2,4-(O2N)2C6H3CHO, reacted readily with H2NCH2CO2Et (II) at room temperature in EtOH. The course of the reaction was followed by ascending paper chromatography with 40:10:50 BuOH-AcOH-H2O, in which the Schiff base of the condensation product hydrolyzes to phenylserine, detected by ninhydrin as well as by o-tolidine (cf. Reindel and Hoppe, C.A. 49, 4459d). II (2.06 g., freshly prepared) and 6.04 g. p-O2NC6H4CHO in 25 ml. absolute alc. heated 2 hrs. at 75°, the cooled mixture filtered, and the product crystallized from absolute EtOH gave 1.3 g. N-p-nitrobenzylidene-β-p-nitrophenylserine Et ester, m. 149-50°, decomposed by addition of HCl to a solution in alc. to β-p-nitrophenylserine Et ester HCl salt, m. 182°. The mother liquor treated with EtOH and HCl, the solution concentrated in vacuo, extracted with H2O, filtered, and the product crystallized from EtOH-EtOAc-Et2O gave the threo-isomer, m. 156-8° (cf. Holland, et al., C.A. 48, 10,680b). Similarly was obtained β-p-(chlorophenyl)serine Et ester HCl salt, m. 183° (from BuOH and EtOH). H2NCH2CONH2 (III) (350 mg.) and 1.4 g. p-O2NC6H4CHO dissolved in 25 ml. absolute alc. at 75°, the solution kept 3 days at room temperature and 12 hrs. at -8°, filtered, and the residue recrystd. from dioxane gave 370 mg. Schiff base of III; the mother liquor yielded 750 mg. 2nd crop, crystallized from HCONMe2 and dioxane to give N-p-nitrobenzylidene-β-p-nitrophenylserinamide, m. 183-5°. The ester group is therefore not essential for the condensation but since glycine esters substituted at the NH2 group failed to react with p-O2NC6H4CHO, a free NH2 group is essential for condensations under these conditions.
IT **99845-20-2**, Cinnamic acid, α-acetamido-2-hydroxy-4-nitro-
(preparation of)

RN 99845-20-2 CAPLUS
CN Cinnamic acid, α-acetamido-2-hydroxy-4-nitro- (6CI) (CA INDEX NAME)

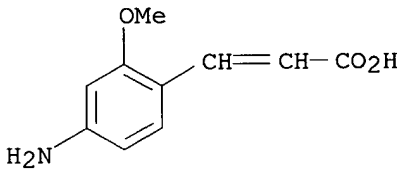


L4 ANSWER 86 OF 92 CAPLUS COPYRIGHT 2005 ACS on STN
ACCESSION NUMBER: 1955:12261 CAPLUS
DOCUMENT NUMBER: 49:12261
ORIGINAL REFERENCE NO.: 49:2505g-h
TITLE: Cinnamic acid derivatives
PATENT ASSIGNEE(S): Cilag Ltd.
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
CH 287557		19531016	CH	<--

AB Substituted cinnamic acid derivs. are produced by the interaction of diazonium salts with CH2:CHCO2H. Thus to 25.2 g. 4,2-O2N(MeO)C6H3NH2 in 350 ml. water and 42 ml. concentrated HCl diazotized with 10.8 g. NaNO2 and cooled to -5° is added 10.8 g. CH2:CHCO2H, 7.5 g. CuCl2, and 70 g. NaOAc, the mixture is stirred overnight, let stand for a day, the precipitate extracted with aqueous NaHCO3, the extract acidified, and purified by C yields 11-14 g. 4,2-O2N(MeO)C6H3CH:CHCO2H, m. 257-8°, reduced with Raney Ni and H in EtOH 6 hrs. at 20° to 8.5 g. 4-H2N analog, m. 160° (decomposition).

IT **195046-20-9**, Cinnamic acid, 4-amino-2-methoxy-
(preparation of)
RN 195046-20-9 CAPLUS
CN 2-Propenoic acid, 3-(4-amino-2-methoxyphenyl)- (9CI) (CA INDEX NAME)



L4 ANSWER 87 OF 92 CAPLUS COPYRIGHT 2005 ACS on STN
ACCESSION NUMBER: 1953:54823 CAPLUS
DOCUMENT NUMBER: 47:54823
ORIGINAL REFERENCE NO.: 47:9298a-e
TITLE: Some syntheses in the p-acetamidobenzaldehyde series
AUTHOR(S): Shchukina, M. N.; Borodina, G. M.; Sazonova, E. D.
CORPORATE SOURCE: S. Ordzhonikidze All-Union Chem.-Pharm. Inst., Moscow
SOURCE: Zhurnal Obshchei Khimii (**1952**), 22, 1659-63
CODEN: ZOKHA4; ISSN: 0044-460X
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

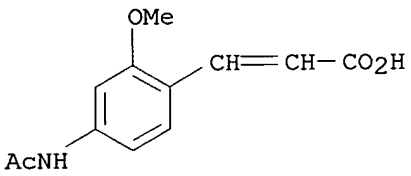
AB To 10 g. 4,2-O2N(MeO)C6H3Me in 40 ml. refluxing EtOH was added in 3 hrs. 6 g. S in 85 ml. 12% NaOH, and refluxing continued 1 hr.; concentration of the solution and treatment with 5% HCl gave 4-amino-2-methoxybenzaldehyde-HCl; this with Ac2O-Ac-ONa and AcOH gave 4-acetamido-2-methoxybenzaldehyde (I), m. 143-4°. The 4-amino analog thiosemicarbazone, m. 163-4°

(from EtOH); I thiosemicarbazone, m. 211-12° (from EtOH). A similar reaction sequence with 4,2-O2N(PhCH2O)C6H3Me gave 4-acetamido-2-benzyloxybenzaldehyde, m. 95-100° (from H2O); thiosemicarbazone, m. 199-201° (from EtOH). The mother liquor from the isolation gave some starting material and a little 4-acetamido-2-benzyloxytoluene, m. 116-20°. Hydrogenation of 4,3-AcNH(O2N)C6H3CHO over Raney Ni in EtOH gave 4-acetamido-3-aminobenzaldehyde-HCl (thiosemicarbazone of the free base, decompose 320°); acetylation of the crude hydrogenation product with Ac2O gave 3,4-diacetamidobenzaldehyde, isolated as the thiosemicarbazone, m. 275-6°. Heating 0.5 g. 4,2-H2N(MeO)C6H3CHO in 10 ml. CHCl3 with 0.4 g. succinic anhydride 1.5 hrs. gave 0.2 g. yellow 4-succinylamido-2-methoxybenzaldehyde, C12H13O5N, m. 193-4° (from dilute EtOH) [thiosemicarbazone, m. 189-90° (from dilute EtOH)]. 4,3-H2N(MeO)C6H3CHO [thiosemicarbazone, m. 160-1° (from EtOH)] similarly gave the 3-MeO isomer, m. 178-9° (from H2O) [thiosemicarbazone, m. 200-1° (from dilute EtOH)]. 4-Acetamido-3-methoxybenzaldehyde thiosemicarbazone, m. 232-3° (from EtOH). Benzoylation with BzCl in 10% KOH gave 4-benzamido-3-methoxybenzaldehyde, isolated as the thiosemicarbazone, decompose 250° (from EtOH). Heating 2 g. I and 1.08 g. malonic acid with 4.5 ml. 8% alc. NH3 and decarboxylating the crude product by heating gave 0.75 g. 4-acetamido-2-methoxycinnamic acid, m. 229-30° (from dilute EtOH). Hydrogenation over Raney Ni gave the hydrocinnamic acid analog, m. 168-9° (from dilute EtOH), which heated with AcOH-HBr 3 hrs. at 140° gave the 4-amino-2-hydroxyhydrocinnamic acid HBr salt, crystals from EtOH-Et2O, m. 189-90°.

IT **856177-27-0**, Cinnamic acid, 4-acetamido-2-methoxy-
(preparation of)

RN 856177-27-0 CAPLUS

CN Cinnamic acid, 4-acetamido-2-methoxy- (5CI) (CA INDEX NAME)



L4 ANSWER 88 OF 92 CAPLUS COPYRIGHT 2005 ACS on STN

ACCESSION NUMBER: 1952:8597 CAPLUS

DOCUMENT NUMBER: 46:8597

ORIGINAL REFERENCE NO.: 46:1542e-i

TITLE: 7-Nitro- and 7-aminocoumarins

AUTHOR(S): Libermann, David; Desnoes, Andre; Hengl, Louis

SOURCE: Compt. rend. (**1951**), 232, 2027-9

DOCUMENT TYPE: Journal

LANGUAGE: Unavailable

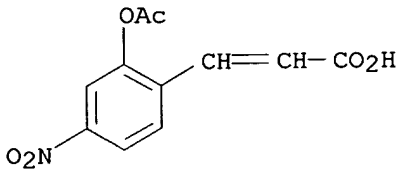
AB Coumarin derivs. were made for trial as bacteriostats. H2SO4 (96 ml.) was slowly added with cooling to 600 ml. Ac2O, 31.3 g. 2,4-HO(O2N)C6H3Me added, the mixture stirred 1 hr., 600 ml. HOAc added, the mixture cooled to 0°, 112 g. CrO3 slowly added, and the mixture stirred 3 hrs. at 5-10° and poured into 5 l. ice to yield 22-24 g. 2,4-AcO(O2N)C6H3CH(OAc)2, which was hydrolyzed to 2,4-HO(O2N)C6H3CHO (I). I (12 g.), 18 g. NaOAc, and 27 g. Ac2O g. were refluxed 3 hrs., cooled, filtered, washed with Ac2O, neutralized with Na2CO3 solution, filtered, the residue refluxed 2 hrs. with 13 g. Na2CO3 in 320 ml. H2O, precipitated with HCl, and recrystd. from 50% HOAc to yield 8 g. 7-nitrocoumarin (II), m. 198-200°. The filtrate obtained after the preliminary neutralization with Na2CO2 was acidified with HCl and the precipitate crystallized from 50% dioxane to yield 1 g. trans-2-acetoxy-4-nitrocinnamic acid, m. 196°, which was saponified to yield 0.5 g. trans-2-HO acid, m. 267°. II (4 g.) was slowly added to a suspension of 8 g. powdered Fe in 130 ml. H2O containing 1.3 g. NH4Cl at 80-90°, the mixture stirred 3

hrs. at 90-100°, cooled, filtered, the Fe extracted with 150 ml. Me2CO, the Me2CO evaporated, and the residue crystallized from EtOH to yield 2.5 g. 7-aminocoumarin, m. 205-6°, forms yellow solns. with blue fluorescence. EtO2CCH2Ac (5.7 g.) in 30 ml. Et2O was added to 1.05 g. Na in 20 ml. EtOH and 30 ml. Et2O, then 10 g. 2,4-AcO(O2N)C6H3COCl in C6H6 and Et2O, the mixture refluxed 1 hr., a 2nd equal portion of Na in EtOH added, the mixture heated 3 hrs., filtered, and the residue acidified with HOAc and crystallized from dioxane to yield 3-acetyl-4-hydroxy-7-nitrocoumarin, m. 201°.

IT **854883-64-0**, Cinnamic acid, 2-hydroxy-4-nitro-, acetate (preparation of)

RN 854883-64-0 CAPLUS

CN Cinnamic acid, 2-hydroxy-4-nitro-, acetate (5CI) (CA INDEX NAME)



L4 ANSWER 89 OF 92 CAPLUS COPYRIGHT 2005 ACS on STN

ACCESSION NUMBER: 1940:12844 CAPLUS

DOCUMENT NUMBER: 34:12844

ORIGINAL REFERENCE NO.: 34:1986a-i,1987a

TITLE: Nitrogen heterocycles. XLVI. 4,6-Diaminoisophthalaldehyde. 3

AUTHOR(S): Ruggli, Paul; Frey, Hugo

SOURCE: Helvetica Chimica Acta (**1939**), 22, 1413-27
CODEN: HCACAV; ISSN: 0018-019X

DOCUMENT TYPE: Journal

LANGUAGE: Unavailable

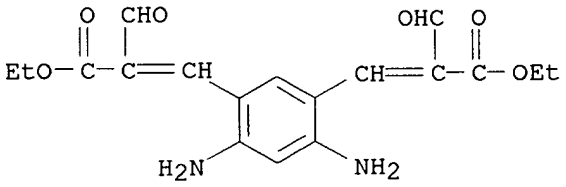
AB The 3,6-dicarboxylic ester produced by the addition of 2 mols. AcCH2CO2Et to 4,6-diaminoisophthalaldehyde (I) was saponified to the free acid which was decarboxylated by heating with Cu in quinoline at 160-230° for 20 min. The resulting 2,7-dimethylbenzodipyridine (II) was converted into the hexa-Br derivative which was transformed by heating with oleum to the crude benzodipyridine-2,7-dicarboxylic acid (III). A mixture of 0.25 g. III, 2 cc. of 10% NH4OH and 2 cc. alc. was triturated, diluted with 20 cc. H2O and heated. The NH3-free product was diluted with 10 cc. H2O and boiled with 0.5 g. AgNO3 in 10 cc. H2O. The crude Ag salt (0.45 g.) was boiled with 70 cc. MeOH and 0.4 g. MeI for 1 h., filtered and concentrated to 20 cc., yielding 0.2 g. (70%) of yellow needles of di-Me benzodipyridine-2,7-dicarboxylate, C16H12N2O4, m. 272° (with darkening). Decarboxylation of III gave benzodipyridine (IV); perchlorate, m. 268° (explosive on rapid heating); MeI derivative, m. above 200° (decomposition). Reduction of 0.2 g. IV in 5 cc. of boiling AmOH with 0.35 g. Na and recrystn. from alc. gave octahydrobenzodipyridine, m. 111.5°, identified through the di-NO and di-Ac derivs., m. 179° (decomposition) and 143°, resp. Reduction of II with Na in AmOH gave as main product a resin which was converted into a colorless crystalline octahydro-2,7-dimethylbenzodipyridine diperchlorate, C14H22Cl2N2O8, m. 285-6° (decomposition). The resinous free base yielded 2 isomeric di-NO derivs., m. 164.5 and 151.5-2.0°, resp. Condensation of 0.2 g. II with 0.5 g. of p-Me2NC6H4CHO at 170-5° in the presence of 10 drops of piperidine produced 0.45 g. of orange-red 2,7-bis(p-dimethylaminostyryl)benzodipyridine, C32H30N4, m. about 340° (with darkening), dissolving in HCl to give violet, blue, green and yellow solns. with increasing acid concns. Condensation of II with o-C6H4(CO2Et)2 by heating in the presence of Na for 14 h. at 100° gave a scarlet crystalline powder which on sulfonation dyed wool and silk bluish red in an acid bath. A unilateral condensation of 0.6 g. I with 6 cc. AcCH2CO2Et occurred on heating in the presence of 9 drops of piperidine for 30 min. at 170°. The impure 3-acetyl-6-formyl-7-

aminocarbostyril yielded yellow crystals of a pure Ac derivative, C14H12N2O4, m. 320-40° (decomposition). Treatment of 1 g. I in 100 cc. alc. at 30° with 14 g. of dry OHCCHNaCO2Et, boiling for 1 h. after standing for 3 days, filtering off the brown amorphous precipitate (V), adding 1 cc. H2O and standing for 8 days gave a Na salt which was dissolved in 50 cc. H2O, acidified with 10% HCl and recrystd. from dioxane, yielding di-Et 2,6-diaminoisophthalaldiformylacetate, C18H20N2O6, m. 250° (decomposition). V was dissolved in H2O, filtered and precipitated with dilute HCl. The amorphous product (0.06 g.) was decarboxylated by heating in vacuo with 0.3 g. BaO and 0.5 g. Cu at 150° to yield a bright yellow sublimate of IV. Condensation of I with excess cyclohexanone in the presence of piperidine produced 2,3,6,7-bis (tetramethylene)-benzodipyridine, C20H20N2, m. 250-1° (with darkening); dipicrate, m. 195° (decomposition). A mixture of 8 g. I in 150 cc. alc., 24 cc. PhCH2CN and 12.5 cc. of 30% NaOH was heated for 30 min. on the steam bath. Working up and purification through the di-HCl salt gave a free base (VI), C24H18N4, m. 301°; tetra-Ac derivative, C32H26N4O4, m. 238.5-9.5° (decomposition). Saponification of VI with HCl produced a carboxyl derivative, C24H18N2O3, which gave a Na salt and a mono-Ac derivative, m. 365°. Condensation of 4 g. of 4,6-dinitroisophthalaldehyde with 8.4 g. of dry PhCH(Na)CO2H by heating with 34 cc. Ac2O and 1.2 g. ZnCl2 for 40 h. at 80° gave a powdery dicarboxylic acid which was esterified through the Ag salt to di-Me 4,6-dinitroisophthalalbis(phenylac etate), C26H20N2O8, m. 152.5-3.5°. Condensation of methazonic acid (VII) with o-H2NC6H4CHO yields 3-nitroquinoline and similarly a cold mixture of VII and I in the presence of a min. of HCl gave 20% of yellow-orange needles of a compound C16H14N6O5, m. 290° (decomposition), of undetd. composition

IT **857578-13-3**, m-Benzenediacrylic acid, 4,6-diamino-α,α'-diformyl-, diethyl ester
(preparation of)

RN 857578-13-3 CAPLUS

CN m-Benzenediacrylic acid, 4,6-diamino-α,α'-diformyl-, diethyl ester (4CI) (CA INDEX NAME)



L4 ANSWER 90 OF 92 CAPLUS COPYRIGHT 2005 ACS on STN

ACCESSION NUMBER: 1939:8734 CAPLUS

DOCUMENT NUMBER: 33:8734

ORIGINAL REFERENCE NO.: 33:1325a-i,1326a

TITLE: Nitrogen heterocycles. XXXV. 4,6-Dinitro- and diaminoisophthalaldehydes. 2. lin-Benzodi-α-picoline and benzodipyridine

AUTHOR(S): Ruggli, Paul; Hindermann, Peter; Frey, Hugo

SOURCE: Helvetica Chimica Acta (**1938**), 21, 1066-83
CODEN: HCACAV; ISSN: 0018-019X

DOCUMENT TYPE: Journal

LANGUAGE: Unavailable

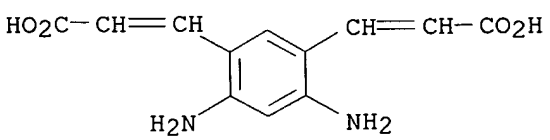
AB cf. C. A. 32, 3394.4. Dinitroisophthalaldehyde (I) (7 g.) in 40 cc. pyridine was warmed to 60°. CO2 and nitrous fumes developed, the temperature rose to 100° and the reaction ended in 45 min. Recrystn. of the resulting 4.8 g. of brown powder gave yellow leaflets, C25H18N2O6, m. above 300°. Other reactions of I with barbituric acid, indandione and methylphenylpyrazolone are cited. The product (0.5 g.) of the reaction between 7 g. I and CH2N2 (C. A. 31, 4287.9) is now considered to be 4,6-dinitrophenylene-1,3-diethylene oxide; C10H8N2O6, m. 153-4°, converted by HCl in pyridine to the corresponding 4,6-dinitrophenylene-1,3-

diethylene chlorohydrin, C10H10Cl2N2O6, m. 150-1°. Boiling 2 g. Et diaminophenylenediacrylate (C. A. 31, 4287.9) with 30 cc. concentrated HCl for 15 min. gave 1.2-1.4 g. of impure 4,6-diaminophenylene-1,3-diacrylic acid HCl salts (II), converted by heating with a 20-fold excess of Ac2O at 120° to the mono-Ac derivative, C14H14N2O5, m. 320° (decomposition). Refluxing with 80 parts Ac2O for 50 min. produced the di-Ac compound, C16H16N2O6, m. 320° (decomposition). The mother liquors of the above saponification yielded yellow matted needles of 7-aminocarbostyril-6-acrylic acid, C12H10N2O3, m. above 300°. Heating 0.5 g. II with 25 cc. concentrated HCl in a bomb-tube for 5 h. at 160° gave, by double ring-closure, 2,7-dihydroxybenzodipyridine, C12H8N2O2, charring above 400°. Most condensations run more smoothly with diaminoisophthalaldehyde (III) than with I, on account of the sensitivity of the latter to alkaline condensation agents. Thus, refluxing 0.65 g. III in 50 cc. alc. and 1 g. barbituric acid in 30 cc. H2O for 10 min. produced 1.4 g. of fine, crystalline orange powder, 4,6-diaminoisophthalaldibarbituric acid, C16H12N6O6, charring above 300°. It is remarkable that no further ring-closure between the adjacent CO and NH2 groups takes place as in the condensation of o-H2NC6H4CHO with barbituric acid. In the presence of 10 drops of KOH in MeOH 0.5 g. III condensed with 5 g. of p-MeOC6H4Ac at 150° to give 0.6 g. of 2,7-di(p-methoxyphenyl)benzodipyridine, C26H20N2O2, m. 268-9°. Condensation of III (2.5 g.) with 10 g. AcCH2Ac in the presence of 15 drops of piperidine in a bomb-tube at 180-90° for 1.5 h. gave 3.5 g. of 2,7-dimethyl-3,6-diacetylbenzodipyridine dihydrate, C18H16N2O2.2H2O, m. 213-15°, converted by heating with Ac2O for 1 h. into an addition compound, C18H16N2O2.Ac2O which, on warming, gave the free base; dioxime, C18H18N4O2, m. 255-7°. III condensed with BzCH2CO2Et by 1-sided ring condensation to 3-benzoyl-6-aldehydo-7-aminocarbostyril, C17H12N2O3, m. 278-9° (decomposition); Ac derivative, C19H14N2O4, m. about 320° (decomposition). The ester resulting from the condensation of III with AcCH2CO2Et in the presence of alc. NaOH (C. A. 31, 4287.9) was saponified and decarboxylated by heating 10 g. of the ester with 75 cc. concentrated HCl in a Durobax bomb-tube (70 cm. by 2.2 cm.; capacity, 270 cc.) up to 130° in 1.0-1.5 h. and for 2 h. at 130°. The crude product gave a high-melting polymer, C14H12N2.2H2O, m. 268°, and 2.8 g. of benzodi-α-picoline (IV), C14H12N2, m. 196-7°; dipicrate, m. 220° (decomposition); monoperchlorate, m. 228-30° (decomposition); diperchlorate, m. 318° (decomposition); chromate; MeI compound, sintering at 244°; dibenzal derivative, C28H20N2, m. 279°; difural derivative, C24H16N2O2, m. 271.5-2.5° (decomposition). Bromination of 4 g. IV in 80 cc. AcOH and 20 g. anhydrous AcONa at 70° with 18.5 g. Br in 40 cc. AcOH with stirring gave 12 g. (90%) of the hexa-Br derivative (V), C14H6Br6N2, m. 190-2° (decomposition), converted by heating with 15% oleum for 50 min. into the corresponding dicarboxylic acid (VI). A mixture of 0.6 g. VI, 2.5 g. Naturkupfer C, 1.8 g. anhydrous Ba(OH)2 and 1.8 g. BaO was sublimed in vacuo at 230-40° and yielded 45% (1.8 g.) of a yellow crystalline sublimate, m. 159-63°. The crude was dissolved in 15 cc. CHCl3 (distilled over K2CO3), filtered and shaken out with 2 cc. of 10% NaOH and with 4 lots of H2O (3 cc.). After drying over MgSO4, treating with charcoal and evaporating, the residue (0.11 g.) was recrystd. from 8 cc. H2O to give snow-white needles of lin-benzodipyridine (1,8-diazaanthracene) , C12H8N2, m. 164.5-5.0°; dipicrate, m. 262° (darkening).

IT **857578-15-5**, m-Benzenediacrylic acid, 4,6-diamino-, (hydrochlorides)

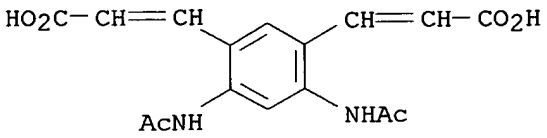
RN 857578-15-5 CAPLUS

CN m-Benzenediacrylic acid, 4,6-diamino- (4CI) (CA INDEX NAME)

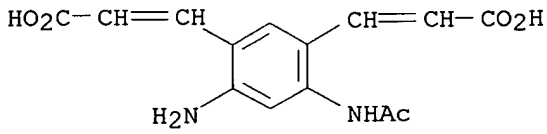


IT **857578-17-7**, m-Benzenediacrylic acid, 4,6-diacetamido-

857578-20-2, m-Benzenediacrylic acid, 4-acetamido-6-amino-
(preparation of)
RN 857578-17-7 CAPLUS
CN m-Benzenediacrylic acid, 4,6-diacetamido- (4CI) (CA INDEX NAME)



RN 857578-20-2 CAPLUS
CN m-Benzenediacrylic acid, 4-acetamido-6-amino- (4CI) (CA INDEX NAME)



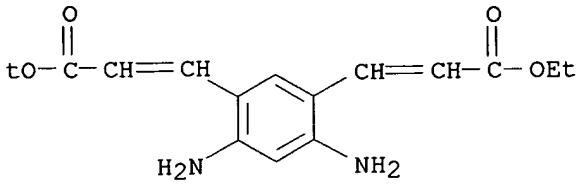
L4 ANSWER 91 OF 92 CAPLUS COPYRIGHT 2005 ACS on STN
ACCESSION NUMBER: 1937:30573 CAPLUS
DOCUMENT NUMBER: 31:30573
ORIGINAL REFERENCE NO.: 31:4287i,4288a-f
TITLE: Nitrogen heterocycles. XXVIII. 4,6-Dinitro-and diaminoisophthalaldehyde. 1
AUTHOR(S): Ruggli, Paul; Hindermann, Peter
SOURCE: Helvetica Chimica Acta (**1937**), 20, 272-82
CODEN: HCACAV; ISSN: 0018-019X
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
AB 4,6-Dinitro-1,3-xylene (100 g.) and 150 g. p-NOC6H4NMe2 were boiled 8 h. in 500 cc. EtOH containing 100 g. anhydrous Na2CO3. Extraction of the crude product with 1.5 l. H2O and then 3 times with 350 cc. Me2CO left 57% of condensation product (I), 100 g. of which was shaken 24 h. with 620 cc. C6H6 (II) and 620 cc. HNO3 (d. 1.12). After filtering off the p-NH2C6H4NMe2.HNO3, the II layer was separated, and concentrated to 100 cc., when 4,6-dinitroisophthalaldehyde (III) (dianil, m. 164.5-65°; disemicarbazone, m. above 360° (decomposition)) crystallized III condenses with compds. containing an active CH2 group. Thus 1.5 g. III in 10 cc. pyridine (IV) was added to 3 g. barbituric acid in 90 cc. hot H2O. After long standing addition of dilute H2SO4 precipitated 4,6-dinitroisophthalaldibarbituric acid. CH2N2 (from 23 g. NO(Me)NCO2Et) in 200 cc. ether was poured over 7 g. III and left 15 h. in the ice box. Long fractional crystallization of the precipitate from EtOH gave 4,6-dinitro-1,3-diacetylbenzene, m. 153-4°. III (20 g.), 100 g. (HO2C)2CH2 and 60 cc. IV were warmed 48 h. at 50-5° and then 2 h. at 100°. Addition of 300 cc. 10% H2SO4 gave 68% of 4,6-dinitrophenylene-1,3-diacrylic acia, m. 216°, after purification through the Et ester (V), m. 116°, and saponification with H2SO4 in dilute AcOH. Reduction of 18 g. V with Rupe's Ni catalyst (VI) gave 14 g. di-Et 4,6-diaminophenylene-1,3-diacrylate, m. 195-6° (di-Ac derivative, m. 244-5°). Reduction of III with VI was unsuccessful. III (16 g.) in 600 cc. EtOH and 360 cc. concentrated NH4OH was dropped with strong stirring during 15 min. into 368 g. FeSO4 in 800 cc. H2O containing a few drops of 10% HCl warmed on the water bath. The Fe precipitate was extracted 15 h. in a Soxhlet with Me2CO (VII) and the residue after removal of VII, boiled with H2O and filtered. On strong chilling 84% of 4,6-diaminoisophthalaldehyde (VIII), m. 208°, separated; dioxime, m. 219-20°; disemicarbazone, chars above 360°; monophenylhydrazone, m. 275-6° (decomposition); diphenylhydrazone, m. 337° (decomposition); mono-Ac derivative, from VIII and Ac2O in the cold for 3 days, m. 270-2°; di-Ac derivative, prepared hot, m. 280-2°. VIII (0.5 g.) in 5 cc. MeCOPh containing 3-4 drops 10%

MeOH-KOH at 100° for 10 min. gave, on precipitation with 50% EtOH, 70% of 2,7-diphenyl-lin-m-benzodipyridine, m. 216-17° (dipicrate, m. 270° (decomposition)). Similar condensation of VIII with AcCH2CO2Et gave di-Et 2,7-dimethylbenzodipyridine-3,6-dicarboxylate, m. 166-7°.

IT **857578-14-4**, m-Benzenediacrylic acid, 4,6-diamino-, diethyl ester
857578-16-6, m-Benzenediacrylic acid, 4,6-diacetamido-, diethyl ester
(preparation of)

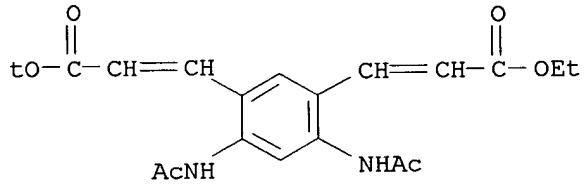
RN 857578-14-4 CAPLUS

CN m-Benzenediacrylic acid, 4,6-diamino-, diethyl ester (4CI) (CA INDEX NAME)



RN 857578-16-6 CAPLUS

CN m-Benzenediacrylic acid, 4,6-diacetamido-, diethyl ester (4CI) (CA INDEX NAME)



L4 ANSWER 92 OF 92 CAPLUS COPYRIGHT 2005 ACS on STN

ACCESSION NUMBER: 1914:11685 CAPLUS
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AUTHOR(S): Lindemann, H.
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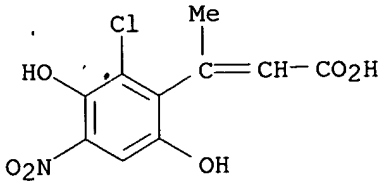
AB 4-Bromoresorcinol bensoate, by the action of 160 g. Br in 80 cc. AcOH upon 214 g. HOC6H4OBz in AcOH, needles, m. 165°. Saponified by b. 10 hrs. with a mixture of equal parts alc. and concentrate HCl, it gives 4-bromoresorcinol (A), C6H4O3Br.o.5H2O, b6 155°; it is very hygroscopic and could not be obtained H2O-free by repeated distns. 4-Methyl-6-bromo-7-hydroxycoumarin, prepared by allowing a mixture of 19 g. (A). 13 g. AcCH2CO2Et and 150 g. H2SO4 to stand 12 hrs., small tables from alc, m. 284°. With K2CO3 and KOH it gives the difficultly soluble yellow salt, whose dilute aqueous solution has a bluish fluorescence. 4-Methyl-8-bromo-7-hydroxycoumarin, from 1.76 g. β-methylumbelliferone (B) in AcOH and 1.6 g. Br, fine needles from alc., M. 204°. With alkaline it gives a yellow salt, easily soluble in H2O. 8-Chloro derivative (C), from 20 g. (B) in AcOH and Cl from 7.45 g. KMnO4, needles from alc., m. 195°. The light yellow alkaline salt is easily soluble in H2O. 6,8-Dichloro derivative, by the use of 15 g. KMnO4, long tables from alc., m. 240°. The yellow alkaline salt is soluble in H2O-with a blue fluorescence. That this is not a keto chloride follows from the facts that it does not liberate I from KI and can be precipitated unchanged from alkaline solution with acids. 3,6,8-Trichloro derivative (D), by the action of an excess of Cl upon a saturated solution of

(B), or by reduction of the keto chloride with SnCl2, m. 268°. The yellow Na salt is soluble in H2O but difficultly soluble in excess of alkaline 4-Methyl-3,5,6,6,8,8-hexachloro-7-keto-5,6,7,8-tetrahydrocoumarin, by saturating (B) in AcOH with Cl and allowing to stand 2 days, prisms, m. 186°. It liberates I from KI, gives (D) when reduced with SnCl2, is only partly decomposed by b. with NaHCO3 in AcOH 2 hrs., gives a yellowish brown solution with b. alkaline, from which acids precipitate a grayish amorphous product. (D) b. 4 hrs. with 15 Parts 33% KOH gives 5,7-dichloro-6-hydroxy-3-methyl-2-coumarilic acid, needles from dilute AcOH, m. 268°, splitting off CO2. Warmed with concentrate H2SO4, it gives a violet solution, gradually becoming deep blue. 4-Methyl-6-nitro-8-chloro-7-hydroxycoumarin, by the action of HNO3 (d. 1.4) on (C) in b. glacial AcOH, long flat prisms, m. 225°. The yellowish red Na salt is soluble in H2O; HCl ppts. the unchanged NO2 compound 4-Methyl-8-bromo-6,?-dinitro-7-hydroxycoumarin, by the use of an excess of HNO3, compact, yellow prisms, m. 236-9°. 4-Methyl-8-amino-7-hydroxycoumarin (v. Pechmann and Obermiller, Ber., 34, 668) may be prepared by condensing 2,1,3-H2N(OH)2C6H3 with AcCH2CO2Et. 4-Methyl-5-chloro-6-hydroxycoumarin (E), from 17.6 g. 4-methyl-6-hydroxycoumarin and the Cl from 6.4 g. KMnO4, large prisms from C6H6, fine, long needles gradually changing to prisms from AcOH, m. 195-201°. It gives yellow alkaline salts, soluble in H2O. 5,7-Dichloro derivative, prisms, m. 246°. 4-Methyl-3,5,5,7,7,8-hexa-chloro-6-keto-5,6,7,8-tetrahydrocoumarin (F), 6-sided tables, m. 138-40°. Upon standing in the air, drying on the H2O bath or warming the AcOH solution with AcONa 0.25 min., it gives 4-methyl-3,5,5,7,8-pentachloro-6-keto-5,6-dihydrocoumarin (G), yellow tables, m. 135-6°. Alkaline gradually dissolves it with a green color (decamp.). Concentrate H2SO4 gives a yellow solution (F), reduced with SnCl2 in AcOH (it need not be isolated), gives 4-methyl-3,5,7-trichloro-6-hydroxycoumarin, needles, m. 197°. Alkaline dissolves it with a yellow color; excess of alkaline ppts. the salt. HNO3 (d. 1.4) oxidizes it to a mixture of 4-methyl-3,7-dichloro- and 4-methyl-3,7,8-trichloro-5,6-coumarinquinones (H). 4-Methyl-3,5,7,8-tetrachloro-6-hydroxycoumarin, obtained by reducing (G) with SnCl2, prisms, m. 227-30°; it gives orange-yellow alkaline salts. HNO3 gives (H). (E) and HNO3 in b. AcOH give 4-methyl-5-chloro-7-nitro-6-hydroxycoumarin, long yellow needles from C4H6, fine needles from AcOH, m. 187° (decamp.). The alkaline salts are red; with excess alkaline the solution becomes bluish violet and the lactone ring is opened. Acidified with HCl, β-methyl-4-nitro-5-hydroxy-6-chloro-2-coumaric acid, yellow prisms from C6H4, compact crystals with 1 mol. H2O from H2O, m. 155° (decamp.). Concentrate H2SO4 gives a yellow solution 4-Methyl-7,8-caumarinquinone , prepared by oxidizing the 7,8-(HO)2 compound with PbO2 in AcMe, red prisms from AcMe, deep red tables with 1 mol. AcOH from glacial AcOH, sinters 175°, m. 200° (decamp.). Na2CO3 gives a deep green color without solution Alkaline partially reduces the compound, also long b. with AcOH, EtOH or H2O, by precipitation of the brown solution in concentrate H2SO4 with H2O, or by sq. H2SO3. 4-Methyl-3,5-6-trichloro-7,8-dihydroxycoumarin. by reduction of the keto chloride, needles from AcOH, m. 245-9° (decamp.). It gives reddish alkaline salts. Oxidized with HNO3 in AcOH it gives 4-methyl-3,7,8-trichloro-5,6-coumarinquione, compact prisms, sinters 200°, m. 270° (decompose). Reduced with H2SO3 it forms 4-methyl-3,7,8-trichloro-5,6-dihydroxycoumarin, needles, sinters 200°, m. 212° (decompose). 4-Methyl-3,5,8-trichloro-6,7-dihydroxycoumarin, needles, m. 225° (decamp.). It forms a yellow sodium salt. Oxidized with HNO2 4-methyl-3,5,8-trichloro-6,7-coumarinquinone results, prism from C6H4, containing C6H4 and 0.5 mol. H2O of crystallization The C6H4 is driven off on the H2O bath, giving a dark brownish red substance, m. 179°. Alkaline dissolves it with decomposition

IT **861577-01-7**, o-Coumaric acid, 6-chloro-5-hydroxy-β-methyl-4-nitro-
(preparation of)

RN 861577-01-7 CAPLUS

CN o-Coumaric acid, 6-chloro-5-hydroxy-β-methyl-4-nitro- (1CI) (CA INDEX NAME)


Cl
Me
HO
C
CH
CO2H
O2N
OH